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Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Semivolatile Industrial Organic Chemicals

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16. ABSTRACT

Previously we reported the development and evaluation of a high-volume air sampler for pesticides and other semivolatile industrial organic chemicals (1). This sampler has proved useful for monitoring airborne pesticides associated with agricultural applcations (2) and polychlorinated biphenyl emissions from incineration and spill cleanup processes (3). Since our initial publication, the sampling system has been improved through redesign of the collection module for more efficient and versatile use. The new module accomodates a reusable sorbent cartridge which can be extracted intact for chemical analysis. Both polyurethane foam (PUF) and granular sorbents can be employed for sampling air at flow rates of 200-250 L/min. This correspondence describes the collection module and reports results of studies conducted to improve sampling efficiencies for more volatile compounds.

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Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Semivolatile Industrial Organic Chemicals

Sir: Previously we reported the development and evaluation of a high-volume air sampler for pesticides and other semivolatile industrial organic chemicals (*1*). This sampler has proved useful for monitoring airborne pesticides associated with agricultural applications (*2*) and polychlorinated biphenyl emissions from incineration and spill cleanup processes (*3*). Since our initial publication, the sampling system has been improved through redesign of the collection module for more efficient and versatile use. The new module accommodates a reusable sorbent cartridge which can be extracted intact for chemical analysis. Both polyurethane foam (PUF) and granular sorbents can be employed for sampling air at flow rates of 200–250 L/min. This correspondence describes the collection module and reports results of studies conducted to improve sampling efficiencies for more volatile compounds.

EXPERIMENTAL SECTION

Apparatus. The modified high-volume pumping system has been previously described (*1*). The new collection module (sampling head) is shown in assembled (b) and exploded configuration in Figure 1. It consists of a milled aluminum housing that holds a glass sampling cartridge (a) and accommodates a 10-cm filter (d) for collection of airborne particulate matter. The module is attached to the inlet of the high-volume pumping system through a tapped and threaded opening ($^1/_2$ in NPT) in the base of the cartridge receptacle (part 1). The sampling cartridge (a) is constructed from a 65 mm o.d. (60 mm i.d.) × 125 mm borosilicate glass cylinder. An indentation 20 mm from the lower end of the cylinder provides a rim to support a 10-mesh stainless steel screen that holds the sorbent. The glass cartridge slips into part 1, part 2 screws down onto part 1, and silicone rubber gaskets (c) cut from GC septum sheet stock provide airtight seals at both ends. The filter is supported by a rimmed 10-mesh stainless steel screen (part 3) that fits into the top of part 2. Part 4 screws into part 2 and is fitted with a silicone rubber "O"-ring (f) to prevent air from leaking around the filter.

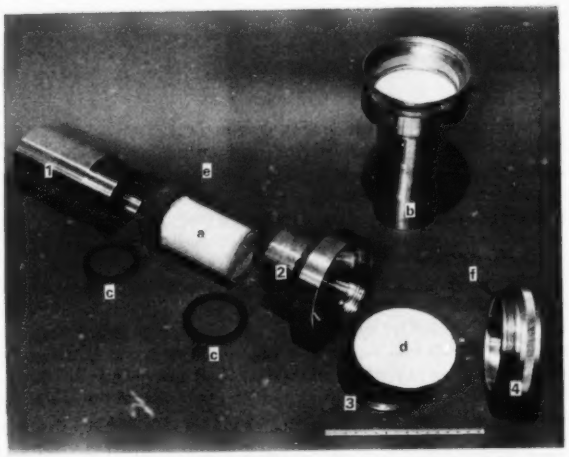

Figure 1. High-volume sampling module: (a) sampling cartridge; (b) assembled module containing cartridge and prefilter; (c) silicone rubber gaskets; (d) glass-fiber prefilter; (e) support screen; (f) silicone rubber "O"-ring; (part 1) cartridge receptacle; (part 2) prefilter adapter; (part 3) filter support screen; (part 4) filter retaining ring.

Materials. Polyurethane foam, polyether-type, density 0.02 g/cm^3 was obtained from Olympic Products Co. (Greensboro, NC). Other sorbents and their sources were Chromosorb 102, 20–40 mesh, Johns-Manville (Denver, CO); Porapak R, 50–80 mesh, Waters Associates, Inc. (Framingham, MA); Amberlite XAD-2, 16–20 mesh, Rohm and Haas, Co. (Philadelphia, PA); Tenax GC, 60–80 mesh, Enka NV (The Netherlands); and Florisil PR Grade, 16–30 mesh, Floridin Co. (Pittsburgh, PA). All pesticides were supplied by the Reference Standards Repository, U.S. Environmental Protection Agency (Research Triangle Park, NC). Chlorobiphenyls were purchased from Applied Science Laboratories (State College, PA). All solvents were "Distilled-in-Glass"

Table I. Collection Efficiencies for Chlorobiphenyls

chlorobiphenyl	calcd air concn, ng/m³	% collected[a] after 24 h at 225 L/min					
		PUF alone	PUF/ Chromosorb 102	PUF/ Porapak R	PUF/ XAD-2	PUF/ Tenax GC	PUF/ Florisil PR
4,4′-di	2.0–20	62	82	82	96	85	111
2,4,5-tri	0.2–2.0	36	80	87	91		92
2,4′,5-tri	0.2–2.0	86	81	89	93	80	88
2,2′,5,5′-tetra	0.2–2.0	94	81	88	88	81	92
2,2′,4,5,5′-penta	0.2–2.0	92	79	92	96	84	97
2,2′,4,4′,5,5′-hexa	0.2–2.0	86	84	92	95	85	93

[a] Average of 6 to 12 determinations.

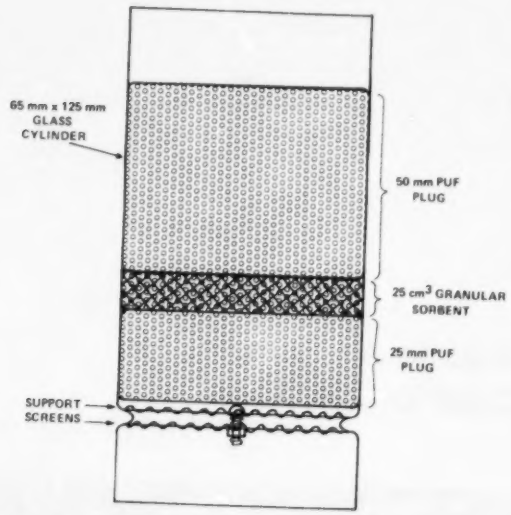

Figure 2. Dual sorbent sampling cartridge.

from Burdick and Jackson (Muskegon, MI).

Collection Efficiencies. Collection efficiencies were determined by vaporizing known quantities of test compounds from a wool-felt mat placed on the filter support (Figure 1, part 3) in a manner similar to that described in our previous paper (*1*). When required, the intake air was filtered through a 102 mm (diameter) × 76 mm PUF trap to remove interfering contaminants. This trap was held in an aluminum receptacle that screwed into the top of part 4 (Figure 1). All sampling periods were 24 h. Residues collected by the sampling cartridge and those remaining on the wool-felt mat (vapor source) were quantified at the ends of the sampling periods. Collection efficiencies were calculated by dividing the weights of the chemicals trapped on the sorbents by the original amounts applied to the felt mat less the residue remaining on the mat. A blank was run with each set of samples, and results were corrected accordingly. Theoretical air concentrations were calculated from the weights of the chemicals vaporized and the volumes of air drawn through the sampling cartridge (usually 300 m³).

Analyses. All sampling media were prepared for use by exhaustive Soxhlet extraction with 5% diethyl ether in hexane as described by Lewis et al. (*1*). After each sampling period, the sampling cartridge was removed from the collection module by gloved hand (latex or polyacetate), wrapped in hexane-rinsed aluminum foil, and stored inside a sealed jar. Within 24 h, the cartridge was placed directly into a 500-mL Soxhlet extractor and extracted for 16 h at 4 cycles/h with 5% diethyl ether in hexane. The filter (or wool-felt mat) was extracted separately in a 250-mL extractor. All extracts were concentrated and analyzed by gas chromatography utilizing electron capture or flame photometric detection as described earlier (*1*). Vacuum drying at 30–40 °C was employed to restore the sorbents for reuse within several hours.

RESULTS AND DISCUSSION

The principal advantage of the collection module described here is that it features a reuseable sampling cartridge which permits the use of either polyurethane foam (PUF) or granular sorbents. While PUF is inexpensive and convenient to use for air sampling, granular sorbents such as Tenax GC and other macroreticular polymeric resins have been shown to trap volatile organic compounds with higher efficiency (*4–6*). These sorbents, however, are generally expensive and exhibit much more air flow resistance than PUF. Therefore, we sought to improve sampling efficiency by combining small quantities of granular sorbents with PUF. By "sandwiching" 25 cm³ of granular sorbent between two 65-mm diameter PUF plugs as shown in Figure 2, flow rates of 200–250 L/min were achievable. The PUF plugs were cut with a 65-mm (i.d.) stainless steel die and fitted under slight compression into the glass sampling cartridges. The sampling cartridges can be extracted, dried, and reused without unloading, permitting costly sorbents such as Tenax GC to be used economically. These dual-sorbent collectors should be efficient at trapping and retaining a broad spectrum of airborne pollutants.

Collection efficiency data for six chlorobiphenyls are given in Table I. Values are averages of at least six replicate determinations (% relative standard deviations 12.5–24.7). 4,4′-Dichlorobiphenyl and 2,4,5-trichlorobiphenyl were trapped more efficiently by all of the PUF-sorbent combinations than by PUF alone. Collection efficiencies were essentially identical for all other, less volatile chlorobiphenyls. There were no notable improvements when the sandwich traps were used for the common organochlorine and organophosphorus pesticides listed in Table II. However, all except diazinon have relatively low volatilities. Poor and variable air sampling efficiencies were encountered for aldrin as has been reported by many investigators using a wide variety of sampling devices (*7*). The PUF-granular sorbent combination would be expected to improve the collection of more volatile pesticides. Recent studies have demonstrated dramatic improvements in sampling efficiencies for several chlorobenzenes when Tenax GC was used in combination with PUF in a similar, low-volume sampling cartridge (*6*).

Repetitive use of the sampling cartridges over long periods of time revealed no problems associated with retention of chemicals or buildup of interfering background material. While an 8-h extraction time at 4 cycles/h was generally adequate, overnight extraction (16 h) was found to be more convenient and assured complete removal of all material from the sorbent. Some migration of the granular sorbents was observed with extended use, particularly for the smaller particle sizes. The useful life for each of the sampling cartridges examined, however, was at least 6 months when put to use two to three times per week.

The major advantage of the trapping system described here is that it permits the economical use of a broad spectrum of

Table II. Collection Efficiencies for Semivolatile Pesticides

pesticide	calcd air concn, ng/m³	% collected[a] after 24 h at 225 L/min					
		PUF alone	PUF/ Chromosorb 102	PUF/ Porapak R	PUF/ XAD-2	PUF/ Tenax GC	PUF/ Florisil PR
aldrin	0.3–3.0	28	34	35	33		40
p,p'-DDE	0.6–6.0	89	83	93	135	71	138
p,p'-DDT	1.8–18	83	77	89	138	69	119
mirex	1.8–18	93	94	95	132	78	123
tech. chlordane	15–150	73	85	74	87	73	97
α-chlordane	1.5–15	114	108	96	102	100	98
γ-chlordane	1.5–15	126	104	91	96	93	100
diazinon	3.0–30	63	72	59	71	76	72
methyl parathion	1.8–18	91	82	72	80	87	83
ethyl parathion	3.6–36	96	85	72	81	86	83
malathion	0.9–9.0	97	88	78	89	91	81

[a] Average 6 to 12 determinations.

sorbent types and combinations for high-volume air sampling. Since 300 m³ or more of air can be sampled in a 24-h period, even relatively poorly trapped chemicals can be accumulated in sufficient quantities to allow reliable measurement of very low air concentrations.

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